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Role of multiple scattering within inverse-photoemission studies of unoccupied molecular adsorbate levels

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An inverse-photoemission study (at $\hbar\omega = 9.7$ eV) of the adsorption of carbon monoxide on a Pd(111) surface is compared with a first-principles calculation of the cross section for the emission of photons as a function of electron angle of incidence. It is found that the calculation is able to explain the experimental results in terms of the relative strengths of the $\sigma \rightarrow \pi$ and $\pi \rightarrow \pi$ channels in the optical transitions.

The adsorption of CO on transition metals is a well established "laboratory" for the study of molecules at surfaces.[1] CO is linearly bonded to the metal surface via the C atom, and bonding occurs by charge transfer between the 5σ CO orbital and the unoccupied metal d bands. This is compensated, as illustrated in Fig. 1, by back transfer from the occupied d bands into the unoccupied CO 2π level. Inverse-photoemission spectroscopy (IPES) promises to be an important new tool in this research area because of its ability to probe the unoccupied levels.[2] Observations of the CO 2π level have already been reported,[3] but so far there have been no direct IPES observations of a peak due to the closely related σ-symmetry shape resonance frequently observed as a final-state effect in photoemission. In this Rapid Communication, we show that the σ shape resonance may be detected indirectly in IPES through its effect in $\sigma \rightarrow \pi$ selection rules. The results illustrate the importance of polarization selection rules in IPES, and are shown to be consistent with first-principles multiple-scattering theory.[4]

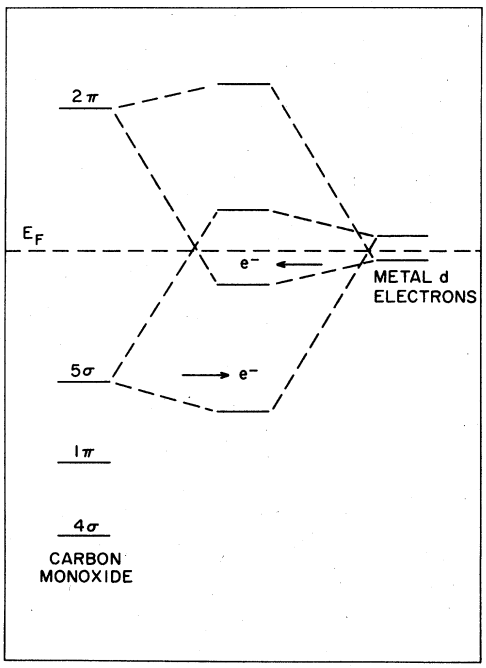

FIG. 1. Bonding and antibonding levels formed in the bonding of a carbon monoxide molecule to a transition-metal surface. Charge transfer from the molecular 5σ level is compensated for by "back transfer" into the unoccupied 2π level.

The technique of inverse photoemission has been discussed elsewhere.[2] The experiments reported here employ a Geiger-Müller counter detecting photons at an energy of 9.7 eV with a spread of approximately ± 0.35 eV. The detector is well removed from the emission point, so as to limit the angular spread in photon collection to $\pm 5°$. The experiments were performed in a Mumetal surface science chamber and surface characterization was monitored by both low-energy electron diffraction (LEED) and Auger electron spectroscopy.

The target was surrounded by a transparent mesh to define uniform electric fields. The photon emission from this mesh provided a constant background which could be used for normalizing intensities between different experimental measurements. The Pd(111) surface was cleaned by cycles of argon bombardment and annealing and the observations from the clean surface will be presented elsewhere.[5] Following cleaning, the Pd surface was exposed to carbon monoxide for typical exposures of 3–5 L (1 L $= 10^{-6}$ Torr sec).

In Fig. 2 comparisons are made between the inverse-photoemission spectra recorded from the clean palladium surface and the same surface following exposure to 5 L of carbon monoxide. Following the adsorption, we note a decrease in the emission from the sp-derived Pd band and the emergence of a new peak at approximately 4 eV above the Fermi level. We associate the new feature with the unoccupied 2π level on the carbon monoxide in agreement with Fauster and Himpsel[3] and note that this peak has reasonably strong emission even for electrons incident along the surface normal. This result is contrary to that expected from a $\sin^2\theta$ dependence as observed previously at higher photon energies.[3] Such a $\sin^2\theta$ dependence will be expected if one assumes a plane wave for the initial state and a final state having p_x, p_y symmetry.[6]

In Fig. 3 we compare the angular dependence of experimentally observed emission intensity with the results of a full multiple scattering theory in which the cross section for the emission of photons of a given energy is calculated as a function of the angle of incidence of the electrons. The theoretical calculation, which will be described in detail else-

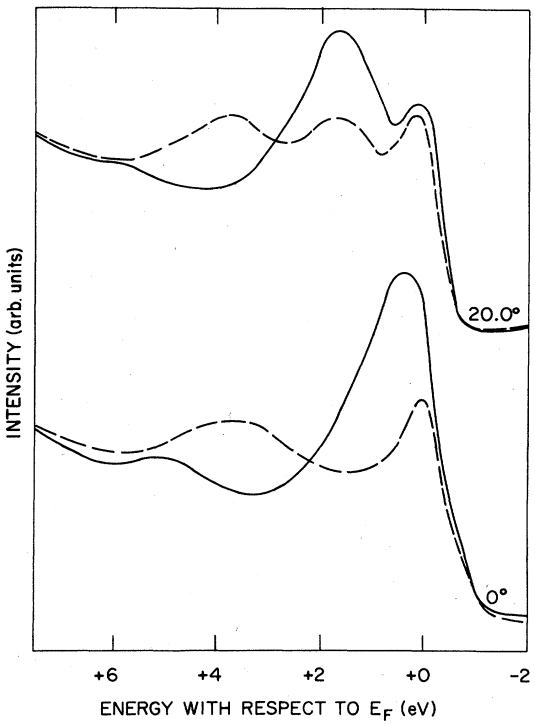

FIG. 2. Inverse-photoemission spectra, as a function of the angle of incidence of the electrons, from a palladium surface before (solid line) and after (dashed line) exposure to 5 L of CO.

where,[4] assumes a carbon monoxide molecule linearly bonded to a single palladium atom via the carbon atom. We believe this cluster model is an adequate description for this system although we note that previous studies of the adsorption of carbon monoxide on the Pd(111) surface indicate a predominance of two and three fold sites.[7] The ground state of the three-atom cluster was calculated self-consistently and the same potential was then used to generate wave functions for the unoccupied (2π) and continuum states. The procedure has been described in detail previously.[8] Using a quantized field treatment it is possible to show that the differential cross section for emission of photons from an isolated cluster is given by

$$\frac{d\sigma}{d\Omega_I} = \frac{\alpha}{2\pi}\frac{\omega}{mc^2}\frac{1}{\hbar k}|\langle b|\hat{\epsilon}\cdot\vec{p}|\psi_k^+\rangle|^2 \ , \qquad (1)$$

where α is the fine-structure constant, $\hbar\omega$ the photon energy, $\hat{\epsilon}$ its polarization, $\hbar k$ the electron momentum, and mc^2 the rest energy of the electron. The matrix element is taken between the bound state $|b\rangle$ and a continuum state with outgoing wave boundary conditions $|\psi_k^+\rangle$. For transitions between the same states it is possible to show that the ratio of the inverse-photoemission cross section to that of photoemission is equal to the ratio of the square of the wavelength of the electron to that of the photon.

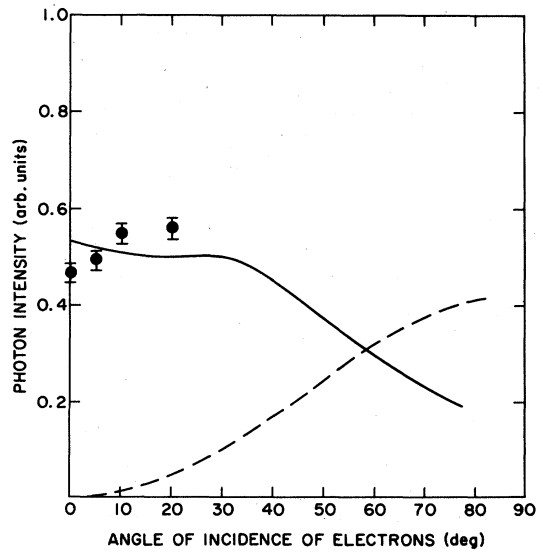

FIG. 3. Comparison of theory (solid line) to experiment (⊕) for a 5-L exposure of carbon monoxide. The dashed line shows the distribution to be expected for a $\sin^2\theta$ dependence with the same electron refraction conditions.

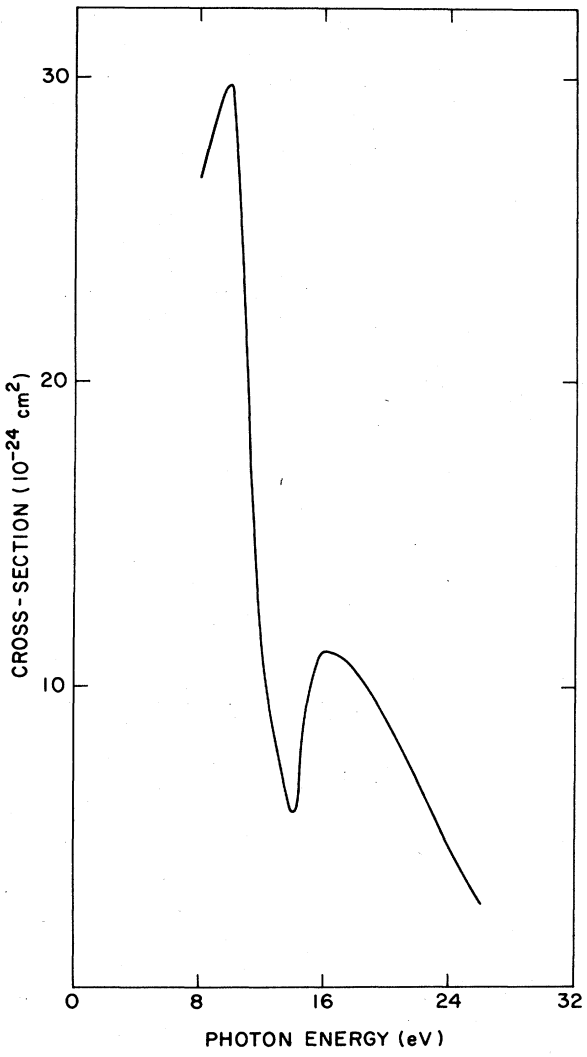

FIG. 4. Calculated cross section for the emission of photons for electrons incident along the molecular axis as a function of emitted photon energy. Photon energy equals incident energy plus experimentally observed binding energy.

The electron incidence angle and the direction of polarization of the emitted photon used in Eq. (1) were modified to account for refraction by the inner potential (taken to be 11 eV) and the dielectric constant of palladium at 9.7 eV. It will be seen in Fig. 3 that the calculation, corrected for area irradiated by the electron beam, accounts nicely for the photon emission observed experimentally with electrons incident near normal. Certain physical constraints in the experimental chamber limited the present experiments to observations within 20° of the surface normal.

In the plane-wave approximation the matrix element is proportional to the Fourier transform of the bound state (in this case the 2π level). Since this vanishes along the molecular axis the large emission observed for $\theta = 0$ must be a non-plane-wave effect. Such effects commonly occur at low kinetic energy where the molecular potential strongly distorts the incident wave. To illustrate this we show in Fig. 4 the cross section as a function of photon energy for electrons incident along the molecular axis. The large peak near 10 eV is due to the well-known σ shape resonance in molecular CO, while the minimum at 14 eV we believe is related to a Cooper minimum. At higher energies the cross section is reduced as the plane-wave treatment becomes a better approximation. It is fortuitous that the fixed photon energy (9.7 eV) of our Geiger-Müller detector should place us within the regime of the shape resonance. It would be desirable in future work to perform normal incidence IPES measurements as a continuous function of $\hbar\omega$, and thereby trace out the profile of the σ shape resonance itself.

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